

Sediment characteristics influencing the bioavailability of nonpolar organic contaminants to *Diporeia* spp.

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ABSTRACT

Organic carbon is considered the major variable affecting the bioavailability of non-polar, sediment-associated contaminants. Previously, variation in bioavailability for some Great Lakes sediments compared to a soil material was nearly a factor of 10 after carbon normalization. Because a soil might not truly represent sedimentary materials, sediments and soils were gathered from several locations in the United States, Canada, and Finland. The accumulation kinetics of the amphipod *Diporeia* spp. were measured for pyrene, benzo[a]pyrene (BaP), 2,4,2',4'-tetrachlorobiphenyl (TCBP), and 2,4,5,2',4',5'-hexachlorobiphenyl (HCBP) sorbed to sediments and soils. The organic carbon content of the sediments ranged from 0.45–21.2% and 32.2–45.0% for soils. The bioavailability, measured as the uptake clearance (amount of source compartment cleared of contaminant per mass of organism per hour), was controlled by the amount of organic carbon, particularly for the chlorinated biphenyls. However, for polycyclic aromatic hydrocarbons (PAH), bioavailability was controlled more by the organic carbon polarity represented by the carbon/nitrogen ratio of the sediment. PAH bioavailability increased as the ratio increased; thus, the more nonpolar the organic matter, the more available the compound. This polarity did not account for any of the chlorinated biphenyl bioavailability. The amount and type of mineral matrix of the sediment did not influence the bioavailability for either compound class. In addition, the amount of oxygen in the sediment was correlated with the bioavailability for BaP after carbon normalization.

Keywords: PAH, PCB, sediment, bioavailability, *Diporeia*

INTRODUCTION

The bioavailability of sediment-associated, nonpolar organic contaminants is reduced by increasing amounts of organic carbon in the sediment (Landrum and Robbins, 1990; Hamelink *et al.*, 1994; and Landrum *et al.*, 1995). Normalization of the exposure to the organic carbon content of the sediment is proposed to address the variability among exposures to sediment-associated contaminants and is the basis for development of sediment quality criteria (Di Toro *et al.*, 1991). However, the literature reveals two anomalies that suggest such normalization is not fully adequate to explain all the variability in bioavailability among and within sediments. First, different classes of compounds, specifically chlorinated hydrocarbons such as polychlorinated

biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), with similar log octanol:water partition coefficients ($\log K_{ow}$) are differentially bioavailable to several benthic organisms when exposed in the same sediment (Landrum and Faust, 1991, 1994; Harkey *et al.*, 1994a). This variability is suggested to occur from both differential partitioning of the various contaminants among several types of sediment particles and, in some cases, differences are augmented by selective feeding (Piérard *et al.*, 1996; Harkey *et al.*, 1994b; Kukkonen and Landrum, 1995, 1996). Second, although variance in bioavailability among sediments is often reduced after carbon normalization, when the uptake rate coefficient is used as an indicator of bioavailability, the residual variance can reach approximately a factor of 10 (Landrum and Faust, 1994). Similar estimates of variability among sediments after carbon normalization, based on calculation of biota sediment accumulation factors (BSAF, organism concentration normalized for lipid content divided by sediment concentration normalized for organic carbon), can also range a factor ten or more (Lake *et al.*, 1990; Lee, 1992).

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These two cited conditions suggest that factors other than the organic carbon content of the sediments contribute to differences in bioavailability. Two additional observations support this hypothesis. Selected PCB and PAH congeners partition differently among sediment particles; and neither class of compounds exhibits a constant ratio between the amount of organic matter in a particular size fraction and the compound concentration (Harkey *et al.*, 1994b; Kukkonen and Landrum, 1995; Evans *et al.*, 1990; Umlauf and Bierl, 1987). Thus, specific interactions may occur between the various organic matter components and the contaminants of interest. Differential sorption has also been demonstrated for these classes of compounds for different chemical fractions of dissolved organic matter (DOM) (Kukkonen *et al.*, 1990). In this case, the chlorinated hydrocarbon representative, 2,2',5,5'-tetrachlorobiphenyl, and the PAH representative, benzo[a]pyrene (BaP), both sorbed to the hydrophobic fraction of the organic matter. BaP sorbed strongly to the hydrophobic acid fraction of the DOM, while the PCB congener had little sorption to that material but was strongly sorbed by the hydrophobic neutral fraction of DOM (Kukkonen *et al.*, 1990). Similarly, the binding CCl_3 and benzene to organic matter decreases with the increasing polarity of the organic matter based on the ratio $(\text{O} + \text{N})/\text{C}$ (Rutherford *et al.*, 1992). The larger the ratio, the greater the number of functional groups on the organic matter and the more polar the natural organic matter. Additionally, for some marine sediments, the percent lipid (organic extractable residue) was found to increase with increasing C:N ratio (McGroddy and Farrington, 1995). Because the sorption of non-polar compounds is, in general, proportional to the lipophilicity of the sorbent, increases in the C:N ratio could represent the relative binding capacity of the sediment.

We hypothesized that the bioavailability of non-polar, sediment-associated contaminants would depend not only on the amount of organic matter in the sediment but also on the type of organic matter and, potentially, on the mineral matrix to which the organic matter is attached. To test this hypothesis, the uptake clearance (amount of contaminant scavenged from the sediment per mass of organism per time) was measured for sediments dosed with selected PAH and PCB congeners. The characteristics of the sediments including the C, N, and O contents of whole sediment, sieved fractions, and extracted DOM, the mineral content of the sediment, and the distribution of the contaminants among the different particle sizes, were measured. The uptake clearance was then compared to the sediment characteristics to determine which factors may have affected the bioavailability.

MATERIAL AND METHODS

Compounds

Two PCB congeners, ^{14}C -2,4,5,2',4',5'-hexachlorobiphenyl (HCBP, specific activity $12.6 \text{ mCi mmol}^{-1}$) and ^{14}C -3,4,3',4'-tetrachlorobiphenyl (TCBP, specific activity 37.1 mCi/mmole), and two PAH congeners,

^3H -benzo(a)pyrene (BaP, specific activity 69 Ci mmol^{-1}) and ^3H -pyrene (PY, specific activity $37.1 \text{ Ci mmol}^{-1}$), were obtained from Sigma Chemical Co., St. Louis, MO. The radiopurity of the compounds was determined using thin layer chromatography (TLC) in hexane:benzene (8:2, V:V) and liquid scintillation counting (LSC) (Landrum, 1988). The radiopurity of each compound was >98% prior to use in the experiments.

Sediments

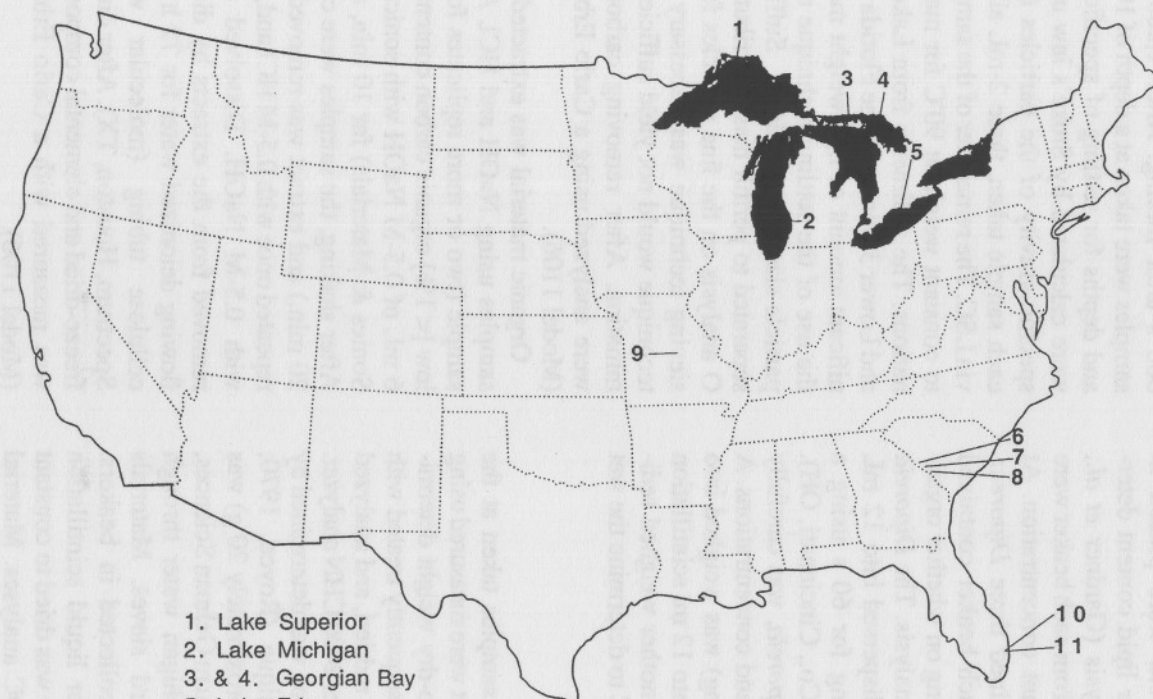
The sediments were obtained from a wide range of geographic sources intended to cover a wide range of potential composition (Figure 1a, b, Table 1). The sediments were shipped wet to the laboratory in polyethylene bottles and held at 4°C until use. All sediments were press sieved through a 1-mm sieve to remove any large debris.

The sediments were dosed as an aqueous slurry of sediment and Lake Michigan surface water by adding the compounds dropwise to the slurry (Landrum, 1989). The compounds were added in an acetone carrier ($0.08 - 0.28 \text{ }\mu\text{L}$ acetone g^{-1} dry sediment). The compounds were added as ^{14}C and ^3H labeled pairs to the sediments. The paired compounds were TCBP with PY and HCBP with BaP. After stirring at room temperature for 4 h, the sediments were returned to 4°C overnight to settle. The supernatant was decanted to remove most of the acetone carrier and fresh lake water was added. The sediments were again mixed with the lakewater and allowed to settle. Settling of particles was not complete for some sediments with overnight settling. The supernatant from these sediments was placed in tubes and centrifuged ($2,000 \text{ g}$) for 30 min at 4°C . The supernatant was removed and the particles returned and remixed into the sediment along with fresh lake water. The sediments were then returned to 4°C and stored for 1–2 days prior to experimental use.

Uptake kinetics

After the storage time, the overlying water was decanted and the sediment mixed for homogeneity. The sediments (20 g) were distributed to 100-mL beakers, 15 beakers per sediment. Samples (approximately 3g) were taken at the beginning, middle, and end of this distribution for later analysis of compound concentrations and for measurement of total organic carbon. Fresh lake water was carefully added to the beakers so the sediment would not be disturbed and the beakers were allowed to stand overnight at 4°C . Five *Diporeia* were added to each beaker and the beakers were sampled after 4, 7, 14 and 28 days for each of the sediments. Exposures were performed for each of the two compound pairs of radio-labeled compounds in each sediment.

On each sampling day, three beakers were chosen for each sediment. The overlying water and any swimming *Diporeia* were removed. The remaining *Diporeia* were recovered by searching through the upper few millimeters of sediment with forceps. The *Diporeia* were placed in a small beaker containing lakewater to wash off any residual sediment. *Diporeia* were taken from the



1. Lake Superior
2. Lake Michigan
3. & 4. Georgian Bay
5. Lake Erie
6. Lower 3 Runs
7. Hollow Creek
8. Savannah River
9. Pond 5, Columbia, MO
10. & 11. Soils

Figure 1. Collection sites for sediments.

Table 1. Whole sediment characteristics measured in Finland

Sediment	Latitude	Longitude	Organic carbon (n) C% \pm SD	Nitrogen (n) N% \pm SD	Hydrogen (n) H% \pm SD	Oxygen (n) O% \pm SD	C/N	(O+N)/C
Lake Superior	48.607 N	88.187 W	0.34 \pm 0.05 (7)	0.021 \pm 0.007 (3)	0.70 \pm 0.06 (7)	4.75 \pm 0.095 (7)	16.2	14.03
Lake Michigan	43.03 N	86.37 W	0.34 \pm 0.07 (11)	0.014 \pm 0.007 (3)	2.24 \pm 0.66 (11)	11.5 \pm 1.9 (11)	24.3	33.9
Savannah River	33.02 N	81.85 W	0.68 \pm 0.14 (4)	0.015 \pm 0.013 (2)	0.94 \pm 0.026 (4)	5.38 \pm 0.82 (4)	45.3	7.93
Pond 5	39.0 N	92.25 W	1.2 \pm 0.2 (4)	0.044 \pm 0.024 (3)	0.70 \pm 0.14 (4)	5.69 \pm 0.61 (4)	26.8	4.86
Georgian Bay 1211	44.764 N	79.871 W	4.8 \pm 1.4 (4)	0.27 \pm 0.12 (4)	1.71 \pm 0.24 (4)	11.2 \pm 0.7 (4)	17.7	2.4
Lake Saimaa	61.138 N	28.135 E	6.0 \pm 0.2 (4)	0.39 \pm 0.03 (4)	2.0 \pm 0.1 (4)	12.0 \pm 1.1 (4)	15.5	2.05
Georgian Bay 1600	44.769 N	79.718 W	6.1 \pm 1.7 (4)	0.32 \pm 0.07 (4)	1.65 \pm 0.14 (4)	7.8 \pm 0.6 (4)	19.1	1.32
Hollow Creek	33.35 N	81.82 W	9.4 \pm 1.7 (6)	0.32 \pm 0.06 (6)	1.3 \pm 0.2 (6)	11.3 \pm 3.1 (4)	29.4	1.23
Lake Erie	42.6 N	80.45 W	11.1 \pm 1.6 (4)	0.75 \pm 0.09 (4)	3.2 \pm 0.2 (4)	21.5 \pm 3.6 (4)	14.7	2.01
Lower 3 Runs	33.07 N	81.47 W	5.84 \pm 0.4 (4) ¹	0.21 \pm 0.04 (4)	0.78 \pm 0.1 (4)	6.6 \pm 1.9 (4)	27.8	0.13
Soil 217 g	26.29 N	80.41 W	33.1 \pm 1.1 (4)	3.0 \pm 0.1 (4)	6.6 \pm 0.2 (4)	29.2 \pm 1.1 (4)	10.9	.97

Analysis of the organic carbon at GLERL yielded essentially the same values for the sediments with the exception of Lower 3 Runs, where the GLERL measure gave C% as 21.2 ± 0.11 . Comparison between the two analyses, excluding Lower 3 Runs, conformed to the following regression $C\% (\text{GLERL}) = -0.15 + 0.97 C\% (\text{Finland})$, $r^2 = 1.0$. Kaolinite releases $10.6 \pm 0.12\%$ oxygen ($n=3$) and $0.048 \pm 0.002\%$ Carbon ($N=3$); Quartz sand released $0.1 \pm 0.03\%$ oxygen.

culture for lipid content at the beginning of the experiment and from experimental beakers on days 14 and 28. At each of the 2 days, 10 animals were taken randomly for lipid determination from among the various sediments. For this analysis, *Diporeia* were placed in preweighed tubes, dried, and their lipid content determined by microgravimetric analysis (Gardner *et al.*, 1985). Two replicates of *Diporeia* from each beaker were prepared to determine contaminant concentration. At least one of the replicates contained three *Diporeia*, while the other replicate from each beaker contained either one or two animals, depending on whether organisms had been removed for lipid analysis. The *Diporeia* were blotted dry, weighed, and dispersed into 12 mL scintillation cocktail by sonicating for 60 s using a Tekmar Sonic Disrupter (Tekmar Co., Cincinnati, OH). A sediment sample, excluding *Diporeia*, was carefully taken for measurement of compound concentrations. A small sediment subsample (100 mg) was weighed into a scintillation vial and dispersed into 12 mL scintillation cocktail by sonication for 90 s. Another weighed sediment subsample was dried at 90°C to determine the wet to dry weight ratio.

Sediment characteristics

Sediment organic carbon (SOC) samples taken at the beginning and end of the experiment were measured using the dried sediment from the wet-to-dry weight determinations. The dry sediment was subsequently treated with 1 N HCl to remove the carbonates, redried, and analyzed for organic carbon on a Perkin-Elmer 2400 CHN analyzer.

Sediment particle-size distribution was determined by a modified sedimentation technique (Royce, 1970; Seibert, 1977). Wet sediment (approximately 20 g) was first wet-sieved using filtered (0.3- μm Gelman Sciences, glass fiber, type A/E) Lake Michigan water through 420-, 105-, and 63- μm standard sieves. Materials remaining on the sieves were collected in beakers. Triplicate samples were taken for liquid scintillation counting (LSC) and the remainder was dried to constant weight at 90°C for mass and SOC analyses. Material

passing the 63- μm sieve was mixed with 1.0 L of filtered Lake Michigan water in a graduated cylinder at room temperature. Samples (25 mL) from the sediment suspension were taken at 20-cm depth at 0, 120, 240, and 600 s after mixing. After 1,200 and 4,600 s, water samples were taken at a depth of 10 cm. Sampling times and depths for settling of specific particle-size classes were calculated by Stoke's law using 2.6 g mL^{-1} as a specific gravity of the particles (Royce, 1970). From each sample taken, three 2-mL aliquots were analyzed via LSC. The remainder of the sample (19 mL) was dried to constant weight at 90°C for mass and SOC determinations. The sediments from Lake Erie, Georgian Bay and Lower 3 Runs, and the Florida soil (217g), had a significant amount of lightweight material that prevented the use of the settling technique to evaluate accurately particle-size distributions. Sufficient material was separated to permit mass distribution and C, H, N, and O analysis on the fine particles for all sediments. The sieving technique was necessary because the settling technique would not yield sufficient mass for the determination. After removing carbonates, these samples were analyzed using a Carlo Erba elemental analyzer (Model 1106).

Organic material was extracted from dried sediment samples using NaOH and HCl. A dry 1.5 g sediment sample (two or more replicates for the samples having low [$< 1\%$] organic carbon content) was extracted using 6 mL of 0.5-M NaOH with sonication (Vibra cell 375; Sonics & Materials) for 10 min, and 24 h on a shaker. After shaking, the samples were centrifuged (4000 rpm 20 min.) and extract was removed. This procedure was repeated once with 0.5-M HCl and, after acid, three times with 0.5-M NaOH. Dissolved inorganic ions were removed from the extracts by dialyzing against overflowing deionized water for 72 h in SpectraSpor® CE cellulose tubing (molecular weight cut-off 500; Spectrum, Houston, TX). After dialyzing, samples were freeze-dried and elemental composition (C, N, H, and O) was measured with a Carlo Erba elemental analyzer (Model 1106).

Another aliquot of each sediment was sieved through a 63- μm sieve and the fine material collected and dried for mineralogy. X-ray diffraction analysis was performed at The University of Michigan with a Phillips diffractometer utilizing scintillation detection, pulse height analyzer, copper radiation, graphite monochromator and theta-compensating slits (D.R. Peacor, University of Michigan, Ann Arbor, MI). The diffractometer was controlled by a micro-computer. The traces were generated at a $1^\circ 2\theta/\text{min}^{-1}$. The intensities of characteristic peaks for each mineral were measured by integrating the area under each peak by planimeter. The approximate 2 θ values are: dolomite 31, calcite 29.5, plagioclase 28, K-feldspar 27.5, quartz 21, illite and muscovite 9, and kaolinite and chlorite 12.5. The weight ratio between a given mineral and quartz was obtained from a calibration curve. The weight percent of each phase was calculated.

Data Analysis

The accumulation data were fit to a first-order accumulation model to estimate the uptake clearance, k_s (g dry sediment g^{-1} organism h^{-1}) as a measure of bioavailability. Most of the exposures for BaP, HCBP, and TCBP were fit to a linear model that assumes that elimination is unimportant (Landrum *et al.*, 1992). For PY, a two-compartment model was required because the assumption regarding elimination was inappropriate based on the shape of the uptake curve (Landrum *et al.*, 1992). Both models assume that the concentration in the sediment remains constant. The data were fit by either linear regression for BaP, HCBP, and TCBP or non-linear curve fitting using the statistical package SystatTM (Wilkinson, 1984). Means and slopes were compared using Students *t*-test. Relationships were considered significant if $p < 0.05$.

RESULTS

Sediment characterization

The bulk sediment characteristics were wide ranging (Tables 1 and 2). These characteristics were determined both at Great Lakes Environmental Research Laboratory, Ann Arbor, MI (GLERL) and at the University of Joensuu, Joensuu, Finland. The two measures produced very comparable results except for Lower 3 Runs sediment, in which was a much lower carbon value was measured in Finland. However, when the sized fractions were examined, the Finland measured carbon content was relatively constant and similar to the higher total organic carbon content measured at GLERL. The soils contained the highest organic carbon content of all the materials. The Lower 3 Runs sediment was very similar to the soils in organic carbon content. Some of the sediments contained small plant fibers as a large portion of their organic carbon content. Among those were Hollow Creek, the soil samples, Lake Erie, and Pond 5 sediments. The mineralogy varied considerably among the various sediments, both in type and amount of the various minerals (Table 3).

Analyses of the sediment fractions for C, N, and O also exhibited a wide range of characteristics (Table 4). Distribution of C, N, and O among the different-sized particle fractions varied considerably and differed from the whole-sediment measures (Table 4). Because *Diporeia* spp. are selective feeders (Harkey *et al.*, 1994b), the characteristics of ingested particles can be considerably different from the characteristics inferred from bulk sediment.

Because *Diporeia* will presumably ingest the organic matter, which in turn is responsible for sorption of the organic contaminants, the relative bioavailability would vary with the composition of the organic matter. In the work of Rutherford *et al.* (1992), the character of the organic matter was defined by the (O+N)/C ratio and partitioning to the organic matter decreased with an increasing ratio. The larger the ratio, the greater the number of functional groups and the more polar the organic matter. However, in the present study when the (O+N)/C ratio was calculated from measured values on whole sediments, the ratio greatly exceeded one due to very high measured oxygen contents (Table 1). This finding suggests an oxygen source other than organic matter and appears to come in part from the sediment clay content. Our control, kaolinite, yielded 16% oxygen. Thus, the ratio of (O+N)/C for bulk sediment or for the sized fractions cannot represent only the polarity of the sediment organic matter, nor can the polarity of the organic matter in sediments be directly evaluated by the method of Rutherford *et al.* (1992). Instead, the polarity was determined by the C/N ratio because N appeared to only come from the organic components of the sediment based on the low percent composition (Table 1 and 4). The larger this ratio, the smaller the number of functional groups and the more nonpolar the organic matter.

In addition to characterizing the solid phase, the organic matter was extracted by traditional humic acid extraction procedures and characterized for C, H, N and O (Table 5). The polarity of these samples could be characterized as had Rutherford *et al.* (1992), because this material was obtained by similar procedures and presumably contained only organic matter after the dialysis treatment.

Differences in the particle composition among the particle-size fractions resulted in differences in contaminant distribution both among the fractions and among the sediments. For example, the relative distribution of pyrene and TCBP exhibited shifts in distribution among particle-size fractions (Figure 2) that were size separated using the settling technique. These differences in contaminant distribution on both an absolute and relative basis are similar to previously observed differences among sediments (Harkey *et al.*, 1994b; Kukkonen and Landrum, 1996). They are thought to contribute to the variance in the bioavailability of sediment-associated contaminants. However, because the contaminant distribution was not measured for all sediments by the same method, *i.e.*, using the settling technique for fine fractions, and because the problem with the settling technique was not recognized prior to experimental

Table 2. Sediment Characteristics Measured at GLERL.

Sediment	Organic carbon % \pm SD	Dry/wet ratio	Volatile solids % \pm SD	Amount fine sediment % \pm SD (<63 μ m)
Lake Superior	0.42 \pm 0.09	0.687 \pm 0.001	2.5 \pm 0.1	24.2 \pm 1.8
Lake Michigan	0.45 \pm 0.03	0.674 \pm 0.003	1.8 \pm 0.4	57.0 \pm 2.7
Savannah River	0.45 \pm 0.03	0.739 \pm 0.003	3.7 \pm 0.1	38.6 \pm 1.2
Pond 5	1.42 \pm 0.04	0.553 \pm 0.006	5.0 \pm 0.03	89.5 \pm 4.6
Georgian Bay 1211	3.89 \pm 0.30	0.244 \pm 0.001	11.7 \pm 0.1	96.0 \pm 1.0
Lake Saimaa	5.49 \pm 0.06	0.147 \pm 0.0004	14.2 \pm 0.2	84.7 \pm 14.7
Georgian Bay 1600	5.62 \pm 0.34	0.364 \pm 0.002	12.8 \pm 0.4	88.7 \pm 0.1
Hollow Creek	9.1 \pm 0.8	0.303 \pm 0.003	21.7 \pm 0.3	47.8 \pm 1.6
Lake Erie	10.6 \pm 0.25	0.236 \pm 0.001	22.8 \pm 1.7	82.4 \pm 1.5
Lower 3 Runs	21.2 \pm 0.11	0.111 \pm 0.01	44.7 \pm 0.2	89.7 \pm 2.9
Soil 217 g	32.2 \pm 0.51	0.096 \pm 0.001	71.2 \pm 0.1	44.9 \pm 2.9
Soil B-2 ¹	45.0 \pm 1.8	0.078 \pm 0.001	85.1 \pm 1.2	46.4 \pm 7.2

^aStation Location 26.36 N latitude and 80.35 W longitude

Table 3. Semi-quantitative XRD analysis of sediment (weight percent)

Sediment	Chlorite mean \pm SD (n)	Illite mean \pm SD (n)	Quartz mean \pm SD (n)	Microcline mean \pm SD (n)	Albite mean \pm SD (n)	Calcite mean \pm SD (n)	Dolomite mean \pm SD (n)	Cummintonite mean \pm SD (n)
Lake Superior	3	5	23	14	44	5	6	0
Lake Michigan	1.3 \pm 0.6 (3)	2.7 \pm 2.9 (3)	26.7 \pm 5.5 (3)	18.3 \pm 0.6 (3)	11.3 \pm 5.9 (3)	5 \pm 1 (3)	34.7 \pm 3.8	1.3 \pm 2.3 (3)
Savannah River	27 \pm 4.2 (2)	16 \pm 2 (2)	44 \pm 0 (2)	5 \pm 2.8 (2)	8.5 \pm 5 (2)	0	0	ND
Pond 5	<1 (2)	2 \pm 1.4 (2)	79 \pm 4 (2)	0	16 \pm 3.5 (2)	4 \pm 1.4 (2)	0	0
Georgian Bay 1211	0	0	31 \pm 2 (2)	27 \pm 6 (2)	35 \pm 5 (2)	0	3 \pm 1 (2)	5 \pm 0 (2)
Lake Saimaa	0	0	40 \pm 7 (2)	18 \pm 7 (2)	40 \pm 3 (2)	2.5 \pm 2.5 (2)	0	ND
Georgian Bay 1600	0	<1	23	33	44	<1	<1	0
Hollow Creek	30	<1	70	0	<1	0	0	0
Lake Erie	2 \pm 1.4 (2)	8 \pm 4 (2)	44 \pm 9 (2)	6 \pm 6 (2)	9 \pm 7 (2)	24 \pm 3 (2)	9 \pm 3 (2)	0
Lower 3 Runs	10 \pm 6 (2)	0	81 \pm 7 (2)	0	2 \pm 2 (2)	7 \pm 4 (2)	0	0
Soil 217g	0	0	0	0	0	96 \pm 1.4 (2)	4 \pm 1.4 (2)	0

The number of replicate analyses is one unless otherwise indicated in parentheses.

ND = not determined, Zero = not detected.

implementation, it was not possible to compare bioavailability among sediments by the relative contaminant distributions on a particle-size basis. However, the C, N, and O measurements were made on all sediments, fractionated using the sieving technique, so the influence of the character of the fractions, as well as the influence of extractable organic matter, on uptake clearance could be explored.

Bioavailability

The uptake kinetics exhibited substantial variation among the sediments for the different compounds. For some specific sediments (Lake Erie sediment and 217g soil) and compounds (BaP and pyrene) the kinetics could not be modeled. These kinetics data were scattered and exhibited neither a linear nor curvilinear pattern over time. The cause of the problem is unclear at this time, but both materials had high organic carbon and contained a substantial amount of small plant fibers (Table 6). As a result, there are no data on the uptake for these two sediments with these two compounds. Surprisingly, the chlorinated biphenyl congeners were not affected.

On a bulk sediment basis, the uptake clearance (k_s), as a measure of bioavailability for the various compounds, varied by approximately a factor of 100 among

the study sediments (Figure 3). There was a general decrease in k_s with increasing log K_{ow} between pyrene and BaP and pyrene and TCBP. The HCBP exhibited a similar k_s to the BaP and TCBP. When the uptake clearance was normalized to the organic carbon content, the variation in bioavailability for each compound among the sediments was reduced to approximately a factor of 10 to 20 (Table 6). Thus, normalizing to the amount of organic carbon in the sediment accounts for a large amount of the variance in bioavailability.

The characteristics of each sediment were examined to attempt to account for the variation in bioavailability among them. It was expected that in addition to accounting for total organic carbon that accounting for other factors, such as the polarity of the carbon components or the inorganic matrix, affecting compound sorption to sediments, might lead to improved understanding of the accumulation of contaminants from sediments. Linear regression analyses were performed with the characteristics of the sediments variable by variable to locate those that might be introducing the most variation for each compound. Multiple variables were not incorporated into the regression analyses because the number of samples in each case was small, 10 or less, and because using multiple variables would not be statistically appropriate

Table 4. Elemental analysis of particle sized fractions.

Sediment	>420 μm mean \pm SD (n)	420–105 μm mean \pm SD (n)	105–63 μm mean \pm SD (n)	63–37 μm mean \pm SD (n)	37–20 μm mean \pm SD (n)	<20 μm mean \pm SD (n)
Lake Superior %C	0.45 \pm 0.17 (3)	0.19 \pm 0.02 (3)	0.17 \pm 0.01 (3)	0.38 \pm 0.02 (3)	1.43 \pm 0.03 (3)	1.74 \pm 0.01 (3)
Lake Superior %N	0.015 \pm 0.002 (3)	0.009 \pm 0.004 (3)	0.008 (0.003 (3)	0.026 \pm 0.001 (3)	0.132 \pm 0.006 (3)	0.18 \pm 0.002 (3)
Lake Superior %O	3.8 \pm 0.02 (3)	3.3 \pm 0.2 (3)	2.5 \pm 0.2 (3)	3.3 \pm 0.4 (4)	4.5 \pm 0.04 (3)	5.9 \pm 0.1 (3)
Lake Michigan %C	1.0 \pm 0.6 (6)	0.24 \pm 0.03 (3)	0.17 \pm 0.01 (3)	0.14 \pm 0.007 (3)	0.30 \pm 0.03 (3)	1.19 \pm 0.32 (3)
Lake Michigan %N	0.013 \pm 0.012 (6)	0.012 \pm 0.004 (3)	ND	ND	0.007 \pm 0.004 (3)	0.078 \pm 0.006 (5)
Lake Michigan %O	1.7 \pm 0.6 (3)	3.1 \pm 0.3 (3)	11.0 \pm 0.7 (3)	18.8 \pm 0.6 (3)	17.9 \pm 1.0 (3)	17.5 \pm 0.3 (3)
Savannah River %C	0.65 \pm 0.07 (3)	0.12 \pm 0.03 (3)	0.19 \pm 0.04 (3)	0.36 \pm 0.01 (3)	0.41 \pm 0.01 (3)	1.23 \pm 0.05 (3)
Savannah River %N	0.028 \pm 0.003 (3)	ND	ND	0.0046 \pm 0.001 (2)	0.009 \pm 0.005 (3)	0.079 \pm 0.013 (3)
Savannah River %O	5.03 \pm 0.08 (3)	0.98 \pm 0.12 (3)	1.86 \pm 0.16 (3)	2.61 \pm 0.11 (3)	3.4 \pm 0.1 (3)	7.99 \pm 0.44 (3)
Pond 5 %C	12.2 \pm 2.2 (3)	3.02 \pm 0.45 (3)	2.18 \pm 0.24 (3)	0.82 \pm 0.15 (3)	0.32 \pm 0.05 (3)	1.35 \pm 0.04 (3)
Pond 5 %N	0.40 \pm 0.04 (3)	0.20 \pm 0.03 (3)	0.13 \pm 0.01 (3)	0.04 \pm 0.01 (3)	0.015 \pm 0.003 (3)	0.12 \pm 0.01 (3)
Pond 5 %O	11.2 \pm 0.1 (3)	6.9 \pm 0.4 (3)	4.4 \pm 0.2 (3)	1.4 \pm 0.1 (3)	1.4 \pm 0.05 (3)	6.4 \pm 0.1 (4)
Georgian Bay 1211 %C	No sample	5.6 \pm 0.3 (3)	4.7 \pm 0.6 (4)	4.6 \pm 0.3 (3)	4.3 \pm 0.1 (3)	3.7 \pm 0.1 (3)
Georgian Bay 1211 %N	No sample	0.48 \pm 0.04 (3)	0.42 \pm 0.08 (4)	0.41 \pm 0.03 (3)	0.41 \pm 0.02 (3)	0.38 \pm 0.02 (3)
Georgian Bay 1211 %O	No sample	10.5 \pm 0.6 (3)	7.1 \pm 1.3 (3)	11.0 \pm 0.6 (3)	11.3 \pm 0.2 (3)	13.0 \pm 0.9 (3)
Lake Saimaa %C	No sample	8.5 \pm 0.1 (3)	6.6 \pm 0.2 (3)	7.9 \pm 0.5 (3)	8.5 \pm 0.1 (3)	4.6 \pm 0.1 (3)
Lake Saimaa %N	No sample	0.96 \pm 0.04 (3)	0.58 \pm 0.02 (3)	0.58 (0.03 (3)	0.59 \pm 0.05	0.39 \pm 0.01 (3)
Lake Saimaa %O	No sample	11.4 \pm 1.0 (3)	8.7 \pm 0.4 (3)	8.5 \pm 0.7 (3)	12.4 \pm 0.1 (3)	8.7 \pm 0.7 (3)
Georgian Bay 1600 %C	No sample	14.7 \pm 1.5 (3)	6.8 \pm 0.8 (3)	14.5 \pm 1.9 (3)	14.4 \pm 0.8 (3)	6.3 \pm 0.01 (3)
Georgian Bay 1600 %N	No sample	0.73 \pm 0.07 (3)	0.27 \pm 0.03 (3)	0.59 \pm 0.07 (3)	0.82 \pm 0.05 (3)	0.49 \pm 0.01 (3)
Georgian Bay 1600 %O	No sample	13.1 \pm 1.7 (3)	10.5 \pm 2.1 (3)	13.8 \pm 0.6 (3)	13.2 \pm 2.8 (3)	10.2 \pm 0.9 (3)
Hollow Creek %C	40.2 \pm 1.8 (3)	5.7 \pm 0.5 (4)	6.6 \pm 0.2 (3)	11.8 \pm 0.6 (3)	9.5 \pm 0.5 (3)	16.0 \pm 0.1 (3)
Hollow Creek %N	1.24 \pm 0.11 (3)	0.20 \pm 0.02 (4)	0.23 \pm 0.02 (3)	0.39 \pm 0.02 (3)	0.44 \pm 0.04 (3)	0.93 \pm 0.03 (3)
Hollow Creek %O	29.2 \pm 2.0 (3)	5.0 \pm 0.4 (3)	4.1 \pm 0.6 (3)	7.7 \pm 0.8 (3)	8.3 \pm 1.3 (4)	13.7 \pm 0.5 (3)
Lake Erie %C	29.7 \pm 0.1 (3)	25.9 \pm 0.5 (3)	17.9 \pm 0.4 (3)	6.5 \pm 0.5 (4)	4.9 \pm 0.2 (3)	8.8 \pm 0.02 (3)
Lake Erie %N	1.92 \pm 0.06 (3)	2.05 \pm 0.03 (3)	1.49 \pm 0.04 (3)	0.53 \pm 0.06 (4)	0.40 \pm 0.03 (3)	0.86 \pm 0.05 (3)
Lake Erie %O	24.2 \pm 1.1 (3)	21.1 \pm 0.2 (3)	19.6 \pm 0.5 (3)	18.6 \pm 0.6 (3)	13.5 \pm 1.1 (4)	16.0 \pm 0.2 (3)
Lower 3 Runs %C	33.4 \pm 4.6 (3)	30.5 \pm 1.2 (3)	26.1 \pm 0.4 (4)	23.4 \pm 0.2 (3)	21.4 \pm 0.2 (3)	16.4 \pm 0.3 (3)
Lower 3 Runs %N	1.42 \pm 0.27 (3)	1.39 \pm 0.09 (3)	1.28 \pm 0.04 (4)	1.13 \pm 0.05 (3)	1.11 \pm 0.03 (3)	0.94 \pm 0.02 (3)
Lower 3 Runs %O	28.3 \pm 0.5 (3)	24.1 \pm 0.8 (3)	21.0 \pm 0.2 (3)	21.2 \pm 0.1 (3)	20.7 \pm 0.1 (3)	17.3 \pm 0.1 (3)
Soil 217 %C	37.5 \pm 1.2 (3)	38.6 \pm 0.2 (3)	38.0 \pm 0.3 (3)	36.7 \pm 0.2 (3)	29.2 \pm 2.4 (3)	27.8 \pm 1.5 (3)
Soil 217g %N	2.76 \pm 0.15 (3)	3.13 \pm 0.05 (3)	3.17 \pm 0.02 (3)	3.15 \pm 0.03 (3)	2.38 \pm 0.18 (3)	2.27 \pm 0.11 (3)
Soil 217g %O	33.5 \pm 0.4 (3)	32.8 \pm 1.0 (3)	32.4 \pm 0.3 (3)	33.8 \pm 0.3 (3)	32.6 \pm 0.9 (3)	31.8 \pm 0.3 (3)

Table 5. Elemental analyses of NaOH extracted organic matter from sediments ($n = 3$).

Sample	C% \pm SD	N% \pm SD	H% \pm SD	O% \pm SD	C/N	(O+N)/C
Lake Michigan	26.34 \pm 1.18	4.07 \pm 0.08	4.03 \pm 0.19	28.32 \pm 0.85	6.47	1.23
Lake Superior	7.18 \pm 0.71	0.88 \pm 0.06	2.63 \pm 0.11	24.63 \pm 0.05 ^a	8.16	3.55
Lake Erie	47.06 \pm 0.12	4.01 \pm 0.04	5.11 \pm 0.08	29.56 \pm 0.14	11.74	0.71
Lake Saimaa	36.52 \pm 0.07	3.12 \pm 0.002	4.74 \pm 0.12	27.92 \pm 0.21	11.71	0.85
Georgian Bay 1211	29.52 \pm 0.18	3.25 \pm 0.03	4.11 \pm 0.02	28.11 \pm 1.43	9.08	1.06
Georgian Bay 1600	36.87 \pm 0.01	2.94 \pm 0.02	4.09 \pm 0.20	29.59 \pm 0.25	12.54	0.88
Pond 5	29.41 \pm 0.06	2.34 \pm 0.004	3.56 \pm 0.19	32.33 \pm 1.46	12.57	1.18
Savannah River	23.04 \pm 1.08	1.98 \pm 0.13	3.37 \pm 0.06	32.62 \pm 1.81	11.64	1.50
Hollow Creek	47.52 \pm 0.18	2.63 \pm 0.01	4.60 \pm 0.06	32.79 \pm 0.27	18.07	0.75
Lower 3 runs	43.48 \pm 0.14	2.45 \pm 0.02	4.46 \pm 0.09	32.10 \pm 0.91	17.75	0.79
Soil 217 gauge	49.84 \pm 0.14	4.43 \pm 0.02	6.37 \pm 0.07	33.08 \pm 0.74	11.25	0.75

^aThe cleanup of this sample was not completely successful at removing the inorganic component. Therefore, the oxygen content may be partially contributed from the inorganic matrix.

with this small sample size. In no case was there a direct linear relationship between k_s and total organic carbon among the sediments (for example BaP, Figure 4). In general, k_s appeared to exhibit an exponential relationship between total organic carbon and uptake clearance. When $\log k_s$ was correlated with the amount of organic carbon, significant negative correlations were found for the two PCB congeners, but not for the PAH congeners (Table 7). However, k_s for pyrene did exhibit a signifi-

cant linear relationship with the amount of organic carbon in both the 37–20- μm and 63–37- μm size fractions (Table 7). These size-fractions were previously shown to be important for accumulation by ingestion and contribute a substantial fraction of bioavailable contaminant from sediment (Harkey *et al.*, 1994b).

For the two chlorinated hydrocarbons, significant negative linear relationships between $\log k_s$ and the amount of carbon in the sediment were most important

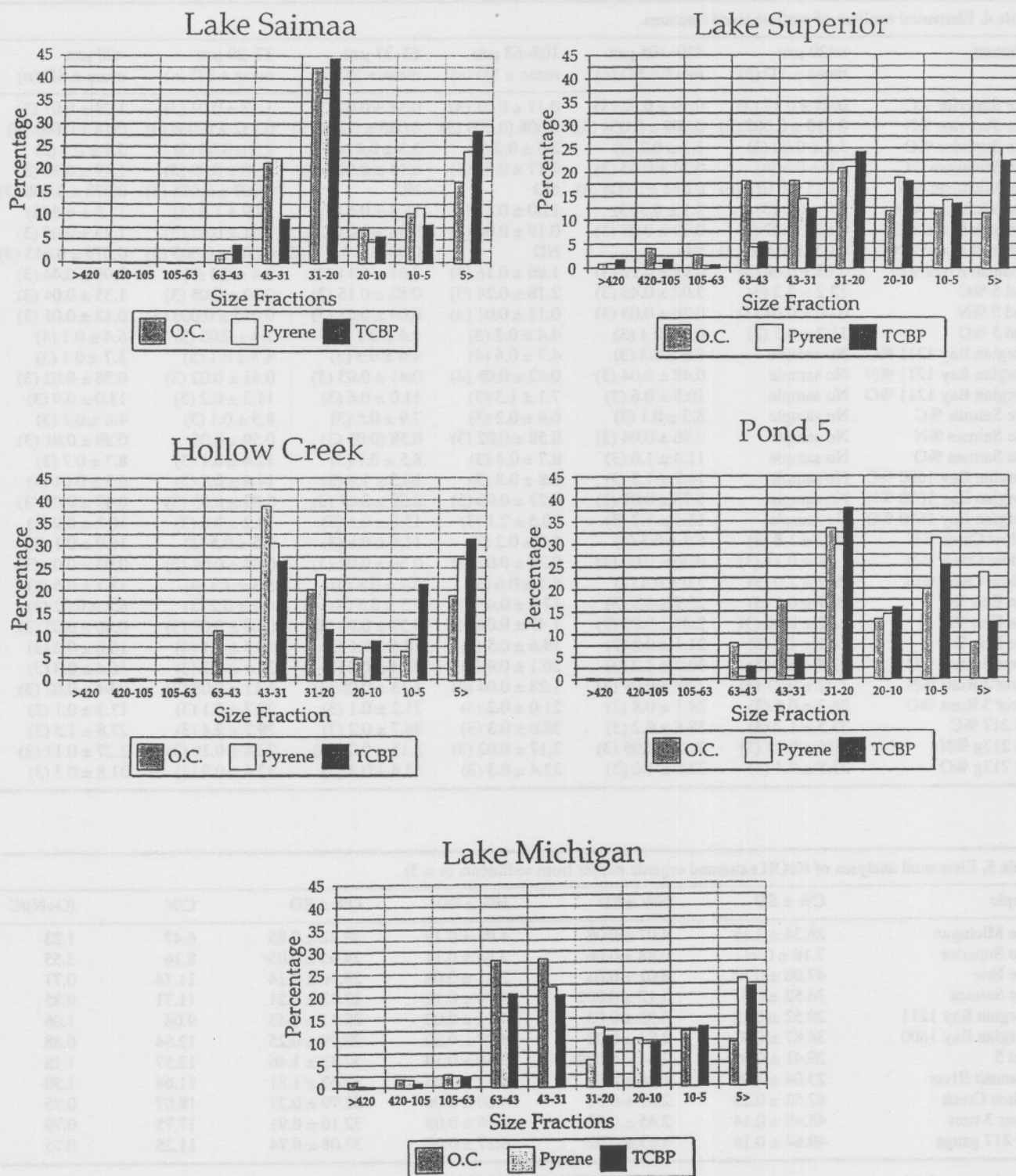


Figure 2. Distribution of organic carbon, pyrene, and tetrachlorobiphenyl among sediment particle-size fractions, where separation was performed using the settling technique.

for describing the variation in the bioavailability. In addition to the relationships between the total organic carbon and $\log k_s$, the two PCB congeners also exhibited significant log-linear relationships between the carbon contents for the 37–20- μm and 63–37- μm fractions (Table 7). The slopes of all the regressions for these relationships were statistically the same for each compound, which suggests that total organic carbon was the driving force (Table 7). Features such as the polarity of

the organic matter, as represented by the C/N ratio, did not seem to have any major influence on the bioavailability of the two PCB congeners. However, for the more hydrophobic HCBP, both the C/N ratio and the (O+N)/C ratio of the extractable dissolved organic matter yielded statistically significant relationships with k_s . As expected, the increasing polarity of the organic matter yielded increasing bioavailability, as measured by k_s (Table 7). In addition, there was a statistically significant

Table 6. Uptake clearance values for *Diporeia* spp. exposed to PCB and PAH congeners.

Sediment	k_s - BaP ¹	k_{soc} - BaP	k_s - PY	k_{soc} - PY	k_s - HCBP	k_{soc} - HCBP	k_s - TCBP	k_{soc} - TCBP
Lake Superior	0.0006	2.5	0.034	100	0.0097	41	0.0238	100
Lake Michigan	0.0029	13.0	0.029	100	0.0043	20	0.002	9.1
Lake Michigan	0.0051	23.0	NM ²	NM	0.0052	24	0.0059	27
Savannah River	0.002	9.1	0.051	200	0.005	22	0.0028	12
Pond 5	0.0008	11.0	0.029	400	0.0097	130	0.0123	180
Georgian Bay 1211	0.0002	7.8	0.0026	100	0.0008	32	0.0008	31
Lake Saimaa	0.0001	6.3	0.0064	400	0.0006	31	0.0006	34
Georgian Bay 1600	0.0005	28.0	0.0037	200	0.0011	63	0.0009	49
Hollow Creek	0.0001	10.0	0.0098	900	0.0014	130	0.0006	51
Lake Erie	NM	NM	NM	NM	0.0019	200	0.0007	71
Lower 3 Runs	0.0003	63.0	0.004	900	0.0003	60	0.0003	63
Soil 217g	NM	NM	ND ³	ND	0.0005	150	ND	ND
Soil B-2	ND	ND	0.0007	300	ND	ND	0.0003	150

¹ k_s has units of g dry sediment g⁻¹ organism h⁻¹; k_{soc} has units of (g organic carbon g⁻¹ organism h⁻¹)

²NM - data could not be modeled.

³ND - experiment not performed

correlation to the percent fines for k_s of HCBP. The negative slope of the correlation suggests that the greater the amount of fines, the more strongly bound and less bioavailable the HCBP. TCBP bioavailability was not well described by measures of polarity or by the fraction of fines; the only significant correlation was log k_s with the (O+N)/C ratio of the extracted organic matter. This correlation hints at the possible role of polarity on bioavailability, but the correlation is not as strong as for the more hydrophobic HCBP.

For the two PAH congeners, the polarity of the carbon was the dominant feature describing the variation in bioavailability among the sediments. The C/N ratio for the 37–20- μ m and 63–37- μ m fractions were significantly positively correlated with k_s for both pyrene and BaP (Table 7). As the C/N ratio increases, the polarity of the organic matter is thought to decrease. Thus, the positive correlation between k_s and the C/N ratio suggests that the organisms ingest the more non-polar material containing contaminant.

For BaP, the carbon normalized uptake clearance (k_{soc}) was correlated with the oxygen content of the sediment (Table 7). Precisely why such a correlation occurred is not clear. The oxygen comes from two potential sources

within the sediment, the organic matter and the clay. The organic matter may contain oxygen from the various functional groups on the molecules. Additionally, when the oxygen was measured for kaolinite clay, 16% oxygen by weight was released. Whether this comes from the clay mineral or from water trapped in the clay is not known. Based on the values measured for the sediments, there was no apparent contribution to the bioavailability from the mineral content. Thus, the reasons for this correlation require further study.

Correlations with measures of polarity for the extracted organic matter were found for both PAH congeners (Table 7). For pyrene which is the least hydrophobic of the two congeners studied, the k_s was strongly correlated with the (O+N)/C ratio and the carbon normalized uptake clearance k_{soc} was strongly correlated to the C/N ratio. Thus, bioavailability as represented by k_s is greater when the polarity of the organic matter increases. Interestingly, when the bioavailability is normalized for the amount of organic matter, bioavailability seems to be inversely related to the polarity of the organic matter. These correlations seem to contradict the observations based on the characterization of the solid phase organic matter. For BaP, the correlations were

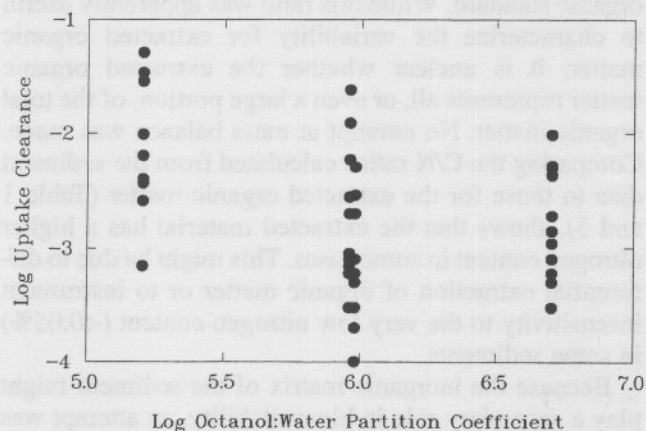


Figure 3. Variation in the uptake clearance for the selected contaminants among the various sediments.

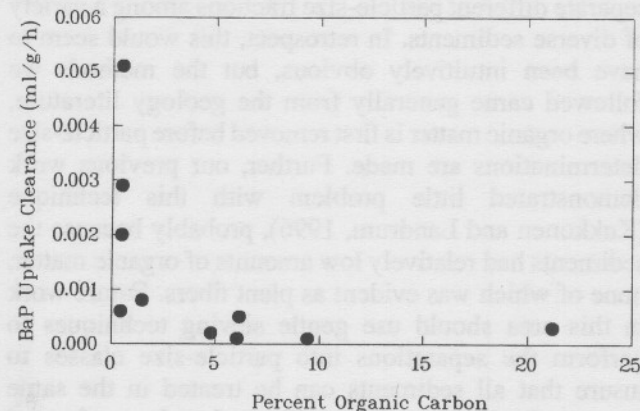


Figure 4. Variation in the uptake clearance for benzo(a)pyrene with increasing organic carbon content of the sediment.

Table 7. Regressions of uptake clearance with sediment characteristics.

Pyrene	
$k_s = 0.029 (0.006) - 0.002 (0.001) C_{63-37\mu m}$	$n=9, r^2 = 0.42, p = 0.04$
$k_s = 0.030 (0.006) - 0.0017 (0.0006) C_{37-20\mu m}$	$n = 9, r^2 = 0.44, p = 0.03$
$k_s = 0.001 (0.008) + 0.001 (0.0006) C/N_{63-37\mu m}$	$n = 8, r^2 = 0.44, p = 0.04$
$k_s = -0.0027 (0.01) + 0.0009 (0.0004) C/N_{37-20\mu m}$	$n = 9, r^2 = 0.36, p = 0.05$
$k_{soc} = -0.005 (0.0001) + 0.00007 (0.00001) C/N_{ext}$	$n = 9, r^2 = 0.85, p < 0.001$
$k_s = -0.048 (0.013) + 0.063 (0.012) (O+N)/C_{ext}$	$n = 8, r^2 = 0.78, p = 0.002$
$k_s = 0.05 (0.013) - 0.0005 (0.0002) \text{Fine}_{<63\mu m}$	$n = 9, r^2 = 0.43, p = 0.03$
Benzo[a]pyrene	
$k_s = -0.0001 (0.0001) + 0.000027 (0.000004) C/N_{63-37\mu m}$	$n = 8, r^2 = 0.85, p = 0.001$
$k_s = -0.001 (0.001) + 0.0001 (0.00002) C/N_{37-20\mu m}$	$n = 10, r^2 = 0.65, p = 0.003$
$k_{soc} = -0.00001 (0.000009) + 0.000003 (0.000001) O_{2\ 37-20\mu m}$	$n = 10, r^2 = 0.56, p = 0.008$
$k_s = 0.004 (0.001) - 0.00025 (0.0001) C/N_{ext}$	$n = 10, r^2 = 0.38, p = 0.05$
$k_s = 0.003 (0.002) + 0.0043 (0.002) (O+N)/C_{ext}$	$n = 9, r^2 = 0.34, p = 0.06$
Tetrachlorobiphenyl	
$\log k_s = -2.4 (0.2) - 0.07 (0.02) C$	$n = 11, r^2 = 0.53, p = 0.007$
$\log k_s = -2.3 (0.2) - 0.06 (0.02) C_{63-37\mu m}$	$n = 11, r^2 = 0.51, p = 0.008$
$\log k_s = -2.4 (0.2) - 0.06 (0.02) C_{37-20\mu m}$	$n = 11, r^2 = 0.47, p = 0.01$
Hexachlorobiphenyl	
$\log k_s = -2.4 (0.14) - 0.038 (0.011) C$	$n = 12, r^2 = 0.50, p = 0.006$
$\log k_s = -2.4 (0.13) - 0.035 (0.009) C_{63-37\mu m}$	$n = 12, r^2 = 0.55, p = 0.003$
$\log k_s = -2.4 (0.12) - 0.044 (0.01) C_{37-20\mu m}$	$n = 12, r^2 = 0.61, p = 0.001$
$k_s = -0.0035 (0.0016) + 0.0055 (0.0016) (O+N)/C_{ext}$	$n = 12, r^2 = 0.54, p = 0.006$
$k_s = -0.0084 (0.018) - 0.00009 (0.00002) \text{Fine}_{<63\mu m}$	$n = 12, r^2 = 0.50, p = 0.006$

Numbers in parentheses represent standard error from the regression.

C = organic carbon content on dry weight basis in whole sediment or specified fraction.

C/N = ratio of the organic carbon content divided by the nitrogen content for whole sediment, the specified particle size fraction, or for the extracted organic matter (ext).

(O+N)/C = ratio of the oxygen content plus nitrogen content divided by the organic carbon content on a dry weight basis for the extracted organic matter (ext)

weaker than those observed for the whole sediment polarity measures and were also opposite to the observed polarity response when solid phase organic matter was characterized (Table 7). Only pyrene of the two studied PAH congeners exhibited a correlation with the percent fines, and the slope indicated that the greater the percent fines, the lower the bioavailability (Table 7).

DISCUSSION

Sediment Characterization

It was clear from the study that methods other than settling techniques are going to be required to properly separate different particle-size fractions among a variety of diverse sediments. In retrospect, this would seem to have been intuitively obvious, but the methods we followed came generally from the geology literature, where organic matter is first removed before particle-size determinations are made. Further, our previous work demonstrated little problem with this technique (Kukkonen and Landrum, 1996), probably because the sediments had relatively low amounts of organic matter, none of which was evident as plant fibers. Future work in this area should use gentle sieving techniques to perform the separations into particle-size classes to insure that all sediments can be treated in the same manner. Such separations will need to be performed gently to prevent disaggregation of organic matter and should be performed in water of similar quality to the collection site to avoid such disaggregations as can

apparently occur in distilled water (Kukkonen and Landrum, 1996).

The organic matter on the solid phase was best characterized by use of the C/N ratio, with no apparent interference from spurious sources as was the case for oxygen. The C/N ratio has been used in other studies for organic matter characterization with some success (McGroddy and Farrington, 1995). The use of the (O+N)/C ratio was not successful for solid phase characterization because of apparent oxygen contribution from some fraction of the inorganic matrix. The inorganic matrix was the assumed source of additional oxygen based on the oxygen measures with kalonite as the inorganic standard. While this ratio was apparently useful to characterize the variability for extracted organic matter, it is unclear whether the extracted organic matter represents all, or even a large portion, of the total organic matter. No attempt at mass balance was made. Comparing the C/N ratios calculated from the sediment data to those for the extracted organic matter (Table 1 and 5), shows that the extracted material has a higher nitrogen content in some cases. This might be due to differential extraction of organic matter or to instrument insensitivity to the very low nitrogen content (<0.05%) in some sediments.

Because the inorganic matrix of the sediment might play a secondary role in bioavailability, an attempt was made to determine the character of the matrix. Because of cost considerations, the measures of the fraction of each of the components had to be on single samples.

However, in an effort to obtain estimates of the variance, replicates were submitted blindly for some of the sediments. The method variation appears to be minimally about 10% and can in many cases be 100%, where the component is in low abundance within the matrix. This variation may partially explain why the inorganic component of the sediment matrix did not appear to contribute to the bioavailability of the contaminants.

The variation in relative distribution among particle-size classes and between sediments for both organic carbon and contaminants has been observed for both laboratory-dosed sediments (Harkey *et al.*, 1994; Kukkonen and Landrum, 1994, 1996) and for field-collected materials (Umlauf and Bierl, 1987; Evans *et al.*, 1990; Piérard *et al.* 1996). The magnitude of distribution difference among particle sizes relative to the organic carbon content for laboratory-dosed systems can be attributed to two possible sources. First, the compounds may not be completely at equilibrium among the organic matter components because of the extent of contact time. The characterization of the sediments and of contaminant distribution were performed after the exposure of the organisms, so the compounds had been in contact with the sediment particles for at least one month, perhaps insufficient time to attain true equilibrium. A second possible explanation for differences in the distributions may be differences in the binding character of the organic matter among the various particles. The C/N ratio varied among particle-size classes within a sediment, typically by about a factor of three and in some cases by as much as a factor of ten. Further, this change in polarity was not an apparent function of particle-size class. Such variation in polar character could easily influence the partitioning and thus, the distribution on a carbon-relative basis similar to the findings of Rutherford *et al.* (1992). Both of the above factors could have influenced the changes in distribution and it is not possible to determine the cause at this time. However, the character of the organic matter is presumed to dominate, because there was a lengthy equilibration before the distributions were determined.

Bioavailability

It is clear from Table 6, that normalization of the uptake data by the organic carbon content does reduce the variability in the range of bioavailability. However, the range still exceeded a factor of 10 in most cases. Only for pyrene could the variability of the organic carbon normalized uptake clearance be accounted for by other characteristics of the sediment. The k_{soc} was positively correlated to the C/N ratio for both the less than 20 μ m particles and for the extracted organic matter. This suggests that the residual variability in bioavailability increased with increasing polarity of the organic matter and in turn that ingestion of nonpolar organic matter in sediments contributes to pyrene accumulation.

Based on the characterization of organic matter for the solid phase, only the amount of organic carbon in the sediment was found to account for the variability in bioavailability of the PCB congeners. As previously

observed (Landrum and Faust, 1994), the relationship between the amount of organic matter and the apparent bioavailability was log linear. Based on measures of the uptake clearance, after the amount of organic carbon exceeds about 1%, the influence of increasing organic matter seems to decline substantially for these non-polar organic compounds. This probably occurs because, assuming a log K_{oc} of 6 at even 1% organic carbon, essentially all the compound (99.99%) is bound to particles.

For these two PCB congeners, the slopes of the regression lines for k_s versus organic carbon content (C) are the same, whether the carbon is for the bulk sediment or for one of the smaller ingestible particle size fractions (Table 7). This suggests that partitioning to interstitial water and subsequent accumulation, rather than ingestion, may dominate the route of uptake for these compounds. This is not to imply that ingestion does not participate as a route for accumulation, but that the water route dominates, as was observed with a study of the assimilation efficiency for HCBP where the fraction that appears to come from ingestion is a maximum of approximately 50% (Kukkonen and Landrum, 1995). Similarly other kinetic studies have suggested that PCB congeners and other chlorinated hydrocarbons are much more available from sediments than are PAH congeners (Landrum and Faust, 1991; Harkey *et al.*, 1994). Thus, these kinetic studies would support the use of total organic carbon to account for differences in bioavailability.

For pyrene, the relationship between bioavailability and the amount of carbon appears to be linear, but the correlations are only significant for carbon concentration measured on ingestible-size fractions. Ingestion has been repeatedly shown or predicted as a dominant route of exposure for accumulation of PAH congeners (Landrum and Robbins; 1990; Kukkonen and Landrum, 1995). While the correlations are significant, they account for only about 40% of the variability in the data and cannot be considered the exclusive factors affecting bioavailability.

One surprising result is the absence of correlation of bioavailability for BaP with carbon in any size-fraction. In fact, the variability in uptake clearance as a measure of bioavailability for BaP is equally large whether carbon normalized or not. Because of the greater hydrophobicity of BaP, it would be predicted that organic carbon should be a more important factor affecting bioavailability than for pyrene. The accumulation of BaP by *Diporeia* seems to be strongly dominated by the ingestion route (Landrum and Robbins, 1990; Landrum and Kukkonen, 1995). The importance of ingestion would be consistent for *Diporeia* because it is an extremely selective feeder (Harkey *et al.*, 1994) and because BaP appears to be more strongly sorbed to sediment particles than can be explained by hydrophobicity alone. This is consistent with studies of BaP bioaccumulation from sediments compared to chlorinated hydrocarbons of similar or greater hydrophobicity (Harkey *et al.*, 1994a; Landrum and Faust, 1990, 1994,

this work). Thus, features of the sediments other than organic carbon alone must be dominant factors affecting BaP bioavailability.

From this work, the dominant factor accounting for differences in bioavailability of the PAH congeners appears to be the polarity of the organic matter in the sediments. This feature accounts for 85% of the variation in the accumulation of BaP. Carbon-polarity may be less dominant for pyrene, because of the lower hydrophobicity of pyrene compared to BaP. There may well be some point at which changes in characteristics of the compounds affect changes in the features that dominate bioavailability. This will need to be determined by examining more compounds with a wider range of characteristics.

CONCLUSIONS

In most cases, the amount of variability in bioavailability that could be accounted for was in the range of 50%. Only single variables were used in the regressions, which may have limited the accounting for variation; larger data sets would have allowed multiple regression. In addition, the short equilibration time before exposure could have minimized the interaction of contaminant and sediment, particularly for the less hydrophobic compounds, and thus reduced the influence of sediment characteristics on bioavailability. Additional equilibration time before exposure may be more realistic and provide a clearer data set. However, in general, the amount of organic carbon dominated bioavailability for PCB congeners while for the PAH congeners the amount of organic carbon is less important. Further, the polarity of the organic matter influenced the bioavailability of the PAH and dominated in the case of BaP. Study of a wider range of sediments should help expand our understanding of the features controlling bioavailability of sediment-associated organic contaminants.

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REFERENCES

- Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals by using equilibrium partitioning. *Environ. Toxicol. Chem.* **10**, 1541–1583.
- Evans, K.M., R.A. Gill and P.W.J. Robotham. 1990. The PAH and organic carbon content of sediment particle size fractions. *Water Air Soil Pollut.* **51**, 13–31.
- Gardner, W.S., W.A. Frez, E.A. Cichocki, and C.C. Parrish. 1985. Micromethod for lipid analysis in aquatic invertebrates. *Limnol. Oceanogr.* **30**, 1099–1105.
- Hamelink, J.L., P.F. Landrum, H.L. Bergman, and W.H. Benson. 1994. *Bioavailability: Physical, Chemical and Biological Interactions*. Lewis Publishers, Ann Arbor.
- Harkey, G.A., P.F. Landrum, and S.J. Klaine. 1994a. Comparison of whole-sediment, elutriate and porewater exposures for use in assessing sediment-associated organic contaminants in bioassays. *Environ. Toxicol. Chem.* **13**, 1315–1329.
- Harkey, G.A., M.J. Lydy, J. Kukkonen and P.F. Landrum. 1994b. Feeding selectivity and assimilation of PAH and PCB in *Diporeia* spp. *Environ. Toxicol. Chem.* **13**, 1445–1455.
- Kukkonen, J., J.F. McCarthy, and A. Oikari. 1990. Effects of XAD-8 fractions of dissolved organic carbon on the sorption and bioavailability of organic micropollutants. *Arch. Environ. Contam. Toxicol.* **19**, 551–557.
- Kukkonen, J. and P.F. Landrum. 1995. Measuring assimilation efficiencies for sediment-bound PAH and PCB congeners by benthic organisms. *Aquat. Toxicol.* **32**, 75–92.
- Kukkonen, J. and P.F. Landrum. 1996. Distribution of organic carbon and organic xenobiotics among different particle size fractions in sediments. *Chemosphere* **32**, 1063–1076.
- Lake, J.L., N.I. Rubinstein, H. Lee II, C.A. Lake, J. Heltshe and S. Pavignano. 1990. Equilibrium partitioning and bioaccumulation of sediment-associated contaminants by infaunal organisms. *Environ. Toxicol. Chem.* **9**, 1095–1106.
- Landrum, P.F. 1988. Toxicokinetics of organic xenobiotics in the amphipod, *Pontoporeia hoyi*: role of physiological and environmental variables. *Aquat. Toxicol.* **12**, 245–271.
- Landrum, P. F. 1989. Bioavailability and toxicokinetics of polycyclic aromatic hydrocarbons sorbed to sediments for the amphipod, *Pontoporeia hoyi*. *Environ. Sci. Technol.* **23**, 588–595.
- Landrum, P. F., and W. R. Faust. 1991. Effect of variation in sediment composition on the uptake clearance of selected PCB and PAH congeners by the amphipod, *Diporeia* sp. In: M. A. Mayes and M. G. Barron (eds), *Aquatic Toxicology and Risk Assessment: Fourteenth*, pp. 263–279. ASTM STP 1124, American Society for Testing and Materials, Philadelphia.
- Landrum, P.F. and J.A. Robbins. 1990. Bioavailability of sediment-associated contaminants to benthic invertebrates. In: R. Baudo, J.P. Giesy, and H. Munteau (eds) *Sediments: Chemistry and Toxicity of In-Place Pollutants*, pp. 237–263. Lewis Publishers, Ann Arbor.
- Landrum, P.F., H. Lee II, and M.J. Lydy. 1992. Toxicokinetics in aquatic systems: Model comparisons and use in hazard assessment. *Environ. Toxicol. Chem.* **11**, 1709–1725.
- Landrum, P.F. and W.R. Faust. 1994. The role of sediment composition on the bioavailability of laboratory-dosed sediment-associated organic contaminants to the amphipod.

- pod, *Diporeia* (spp.). *Chem. Speciat. Bioavail.* **6**, 85–92.
- Landrum, P.F., G.A. Harkey, and J. Kukkonen. 1995. Evaluation of organic contaminant exposure in aquatic organisms: The significance of bioconcentration and bioaccumulation. In: M.C. Newman and C.H. Jagoe, (eds), *Ecotoxicology: a Hierarchial Treatment*, pp. 85–131, Lewis Publishers, Ann Arbor.
- Lee II, H. 1992. Models, muddels, and mud: Predicting bioaccumulation of sediment-associated pollutants: In: G.A. Burton, (ed.), *Sediment Toxicity Assessment*, , pp. 267–293, Lewis Publishers, Ann Arbor.
- McGroddy, S.E. and J.W. Farrington. 1995. Sediment pore-water partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. *Environ. Sci. Technol.* **29**, 1542–1550.
- Piérard, C., H. Budzinski and P. Garrigues. 1996. Grain-size distribution of polychlorobiphenyls in coastal sediments. *Environ. Sci. Technol.* **30**, 2776–2783.
- Royse, C.F. 1970. *An Introduction to Sediment Analysis*. Arizona State University, Tempe, AZ, 180pp.
- Rutherford, D.W., C.T. Chiou, and D.E. Kile. 1992. Influence of soil organic matter composition on the partition of organic compounds. *Environ. Sci. Technol.* **26**, 336–340.
- Siebert, P.C. 1977. Simple sedimentation methods, including the Andreason pipette and the Chan sedimentation balance. In: J.D. Stockham and E.G. Fochman, (eds), *Particle Size Analysis*, Ann Arbor Science, Ann Arbor, pp. 44–55.
- Umlauf, G. and R. Bierl. 1987. Distribution of organic micropollutants in different size fractions of sediment and suspended solid particles of the River Rotmain. *Z. Wasser. Abwasser. Forsch.* **20**, 203–209.
- Wilkinson, L. 1990. *SYSTAT: The System for Statistics*. Evanston, IL, SYSTAT Inc.

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